XI CBSE

CHEMISTRY — CHEMICAL THERMODYNAMICS

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Convection
The transfer of heat from one region of a fluid to another due to movements within the fluid is called convection.

Conduction
The movement of heat within an object is called conduction. Conduction also occurs when objects are touching.

CHEMICAL THERMODYNAMICS

Radiation
Radiation is the transfer of energy through electromagnetic waves.

CHEMICAL THERMODYNAMICS

Chemical Thermodynamics (central node)

$\Delta_r H$ is the enthalpy change per mole of a substance when it undergoes combustion and all reactants and products are in standard state.
(Standard Enthalpy of combustion)

$\Delta_a H$ is the enthalpy change on breaking one mole of bonds completely to obtain atoms in gas phase.
(Enthalpy of atomization — $\Delta_a H^0$)

Property which does not depend on the quantity or size of matter present in the system. Temperature density, pressure.
(Intensive property)

Property whose value depends in the quantity or size of matter present. (Temperature density: Pressure).
(Extensive Property)

Σbond enthalpies reactants – Σbond enthalpies products
(Terms:)

- Systems and surroundings: A system refers to that part of universe in which observations are made and remaining universe constitutes the surroundings.
- **Types of System:**
1. **Open System:** There is exchange of energy and matter between system and surroundings.
2. **Closed System:** There is no exchange of matter but exchange of energy is possible.
3. **Isolated System:** There is no exchange of energy or matter between the system and surroundings.
4. **State of system** : is described by its measurable or macroscopic properties.
5. **Internal Energy** : as a state function: It is the sum of chemical, electrical, mechanical or any other type of energy.
6. **(a) Work**:
Adiabatic process is in which there is no transfer of heat between system and surroundings.
$\Delta U = U_2 - U_1 = W_{ad}$
(b) Heat is change in internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. q is positive: Heat is transferred from surroundings to system. q is negative: Heat is transferred from system to surroundings.
(c) General Case
First law of Thermodynamics: $\Delta U = q+w$ the energy of an isolated system is constant.

In calorimetry, the process is carried out in a vessel called calorimeter, immersed in a known volume of a liquid.
(a) ΔU measurements: The energy changes are measured at constant volume. No work is done.
(b) ΔH measurements: In exothermic reaction, heat is evolved, so q_p and $\Delta_r H$ will be negative. In endothermic reaction, heat is absorbed, so q_p and $\Delta_r H$ will be positive.
(Measurement of ΔU and ΔH)

$Work = P_{ex}\Delta V = -P_{ex}\,(V_f - V_i) = \int_{V_i}^{V_f} P_{ex}dV$
Reversible Process: The process which can be reversed at any moment by an infinitesimal change.
Irreversible Process: Processes other than reversible process.
At constant temperature $W_{rev} = 2.303\ nRT\ \log\dfrac{V_f}{V_i}$
For adiabatic change, $q=0$, $\Delta U = W_{ad}$

(Applications)

(Enthalpy, (H))

(Heat Capacity)

(Entropy)

ΔH is negative: Exothermic reactions.
ΔH is positive: Endothermic reactions.

$q = C\ x\ m\ x\ \Delta T = C\Delta T$

Enthalpy Change, $\Delta_r H$ – Reaction Enthalpy

$\Delta_r H = \Sigma a_i H_{products} \dfrac{-\Sigma}{i} b_i H_{reactants}$
(a) Standard Enthalpy of reactions is the enthalpy change for a reaction when all the participating substances are in their standard states.
(b) Enthalpy changes during phase transformations: Standard enthalpy of fusion / molar enthalpy of fusion, $\Delta_{fus}H^0$ is the enthalpy change that accompanies melting of one mole of a solid substance in standard state. Standard enthalpy of vaporization or molar enthalpy of vaporization. $\Delta_{vap}H^0$ is the amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure.
(c) Standard molar enthalpy of formation $\Delta_f H^0$ is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation.

(Hess's Law of Constant Heat Summation)

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of standard enthalplies of international reactions into which the overall reactions may be divided at the same temperature.

$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots\ldots\ldots$

A → C (via $\Delta_r H_1$)
A → B (via $\Delta_r H_1$)
B → D (via $\Delta_r H_2$)
D → C (via $\Delta_r H_3$)

(Enthalpy of Solutions)

$\Delta_{sol}H^0$ is the enthalpy change when one mole of a substance dissolves in a specified amount of solvent.

(Gibb's Energy)

$*\Delta G = \Delta H - T\Delta S$
ΔG is <0, process is spontaneous.
$*$ ΔG is >0, process is non-spontaneous.

(Lattice Enthalpy — $\Delta_L G^\circ = -RT\ \ln k$)

is the enthalpy change when one mole of an ionic compound dissociates into its ions in gaseous state.

A spontaneous process is an irreversible process which may be reversed by some external agency.

$\Delta S_{total} = \Delta S_{systems} + \Delta S_{surroundings}$
$\Delta = \dfrac{q_{rev}}{T}$

CHEMICAL THERMODYNAMICS

BASIC CONCEPTS

1. **Thermodynamics:** It is the study of flow of energy. It encompasses the study of flow of heat as well as mass.

2. **Thermodynamics Terms:**

   (a) **System:** A system is that specific part of the universe which is under experimental study and separated from surroundings by a boundary.

   (b) **Surroundings:** The part of the universe other than the system which is in a position to exchange energy and matter with the system is termed as surroundings.

   (c) **Boundary:** The real or imaginary surface separating the system from the surroundings is termed as boundary *i.e.*, a boundary refers to the limits of the system.

3. **Types of the System**

   (a) **Open system:** The boundary of this type of a system is **open and non-insulated**. Therefore, an open system can exchange matter as well as energy with the surroundings. For example, tea in a cup or solution of $CuSO_4$ in a beaker.

   (b) **Closed system:** A system that can exchange energy but cannot exchange matter with the surroundings is called a **closed system.** Such a system is non-insulated but sealed. For example, when I_2 is heated in a sealed container, solid iodine sublimes to iodine vapours but iodine vapours cannot escape from the container.

   (c) **Isolated system:** A system which can neither exchange matter nor energy with the surroundings is **called an isolated system.** Such a system is insulated and sealed *e.g.*, pieces of ice in a thermos flask.

4. **The State of the System:** The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T, U, H, S, G, etc. are called state variables or state functions because their values depend only on the state of the system and not on how it is reached. However, W, q are called path functions as their values is affected by the path followed.

5. **The Internal Energy as a State Function:** The total energy of the system whether it may be chemical, electrical, mechanical or any other type of energy, the sum of all these is the energy of the system and it is termed as the internal energy, U of the system, which may change, when

   (i) heat passes into or out of the system,

   (ii) work is done on or by the system,

   (iii) matter enters or leaves the system.

   The change in internal energy can be achieved by changing the state of the system. If U_A and U_B are the internal energies of the system A and B, respectively. Then change in internal energy can be represented as

   $$\Delta U = U_B - U_A$$

6. **Heat (q):** Energy is exchanged as heat between the system and surroundings if they are at different temperatures. A system at a higher temperature loses heat to the surrounding causing a fall in temperature of the system and consequently rise in temperature of the surroundings. This process continues till the temperatures of the two become equal. Likewise, if temperature of the system is lower than that of the surroundings, then heat is gained by the system. According to IUPAC conventions,

Heat absorbed by the system = $+q$

Heat evolved by the system = $-q$

7. **Work (w):** It is the mode of energy transfer to and from the system with reference to the surroundings. If an object is displaced through a distance of dx by a force F, then the amount of work done is given as

$$w = F \times dx$$

It is a path-dependent function.

(a) Work done in irreversible process:

$$w = -p_{ex}(V_f - V_i)$$

Where p_{ex} = external pressure

V_f = final volume

V_i = initial volume

(b) Work done in reversible process: If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

$$w = -\int_{V_i}^{V_f} p_{ex} dV$$

(c) Work done during free expansion: Expansion of a gas in vaccum ($p_{ex} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

According to IUPAC conventions,

Work done on the system by surroundings, $w = +p\Delta V$

Work done by the system on surroundings, $w = -p\Delta V$

8. **First Law of Thermodynamics:** If a change of state is brought about both by doing work and by transfer of heat, then change in internal energy for this case can be written as $\Delta U = q + w$.

The equation i.e., $\Delta U = q + w$ is a mathematical statement of the first law of thermodynamics, which states that **"the energy of an isolated system is constant"**. It is commonly stated as the **law of conservation of energy i.e., energy can neither be created nor be destroyed.**

Note: $\Delta U = q + w$ is a state function but q and w is a path function.

9. **Conclusions from First law of Thermodynamics:** Now, we can write equation $\Delta U = q + w$ in number of ways depending on the type of processes.

Let us substitute $w = -p_{ex} \Delta V$ in equation, and we get

$$\Delta U = q - p_{ex}\Delta V$$

If a process is carried out at constant volume ($\Delta V = 0$), then

$$\Delta U = q_V$$

the subscript V in q_V denotes that heat is supplied at constant volume.

Isothermal and Free Expansion of an Ideal Gas: For isothermal (T = constant) expansion of an ideal gas into vacuum; $w = 0$ since $p_{ex} = 0$. Also, Joule determined experimentally that $q = 0$; therefore, $\Delta U = 0$.

Equation, $\Delta U = q + w$ can be expressed for isothermal irreversible and reversible changes as follows:

(i) For isothemal irreversible change, $q = -w = p_{ex}(V_f - V_i)$

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(ii) For isothermal, reversible change, $q = -w = nRT \ln \dfrac{V_f}{V_i}$

$$= 2.303 \, nRT \log \dfrac{V_f}{V_i}$$

(iii) For adiabatic change, $q = 0$

$$\Delta U = w_{ad}$$

10. Enthalpy, H:

(a) **A Useful New State Function:** In isothermal processes the total energy of the system at constant pressure is given by another thermodynamic function known as **enthalpy** or heat contents of the system. It is represented by H. Mathematically, enthalpy is related to internal energy by the equation

$$H = U + pV$$

where U is the internal energy, p and V are pressure and volume of the system respectively. Therefore, the enthalpy of a system may be defined as the sum of internal energy and the product of pressure and volume of that system.

Enthalpy is a **state function** and is also known as heat content of the system (or substance).

(b) **Enthalpy change (ΔH):** Like internal energy, it is not possible to determine the absolute value of enthalpy (H) of the system. However, the change in enthalpy (ΔH) between the reactants and products is significant for a chemical reaction and can be experimentally measured.

For a chemical reaction, the change in enthalpy (ΔH) can be represented by the relationship

$$\Delta H = [\text{Heat contents of products}] - [\text{Heat contents of reactants}]$$

or $\qquad\qquad \Delta H = H_P - H_R$

Significance of Enthalpy Change: According to the definition of enthalpy, it is related to internal energy by the expression.

$$H = U + pV$$

and the change in enthalpy (ΔH) is given by

$$\Delta H = \Delta U + \Delta(pV)$$
$$\Delta H = \Delta U + p\Delta V + V\Delta p$$

During the process if pressure is constant *i.e.*, change in pressure. $\Delta p = 0$, then the equation becomes

$$\Delta H = \Delta U + p\Delta V$$

Substituting the value of $\Delta U = q - p\Delta V$, we get

$$\Delta H = q - p\,\Delta V + p\,\Delta V$$
$$\Delta H = q_p$$

where subscript (p) means at constant pressure.

Thus, enthalpy change of a system is equal to the heat absorbed or evolved by the system at constant pressure.

(i) **Exothermic reactions:** The reactions which are accompanied with the evolution of heat are called exothermic reactions.

(ii) **Endothermic reactions:** The chemical reactions which are accompanied with absorption of heat are called endothermic reactions.

    1. For exothermic reactions, $\qquad\qquad \Delta H$ or $\Delta U = -$ ve

    2. For endothermic reactions, $\qquad\qquad \Delta H$ or $\Delta U = +$ ve

        At constant volume ($\Delta V = 0$), $\Delta H = \Delta U$ and as $\Delta H = q_p$

      $\therefore \ \Delta U = q_v$

(*iii*) **Relationship between ΔH and ΔU:** The difference between ΔH and ΔU is not usually significant for systems consisting of only solids and/or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved. Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products , n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$$pV_A = n_A RT$$

and $$pV_B = n_B RT$$

Thus, $$pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A)RT$$

or $$p(V_B - V_A) = (n_B - n_A)RT \quad \text{or} \quad p\Delta V = \Delta n_g RT$$

Here, Δn_g refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of $p\Delta V$, we get

$$\Delta H = \Delta U + \Delta n_g RT$$

This equation is useful for calculating ΔH from ΔU and vice versa.

11. **Extensive and Intensive Properties**

   (*a*) **Intensive properties:** The state functions (state variables or stable parameters) of the system which are independent of the quantity of the substance present in the system are called intensive properties. For example, pressure, temperature, concentration, density, viscosity, surface tension, refractive index and specific heat, etc.

   (*b*) **Extensive properties:** The state variables which depend upon the quantity of the substance present in the system are termed as extensive variables. For example, Volume, mass, internal energy, enthalpy, entropy and work are examples of extensive properties.

12. **Measurement of ΔU and ΔH (Calorimetry):** We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions:

   (*a*) **ΔU Measurements:** For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter.

   (*b*) **ΔH Measurements:** Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter.

13. **Enthalpy Change, $\Delta_r H$ of a Reaction – Reaction Enthalpy:** In a chemical reaction, reactants are converted into products and is represented by,

$$\text{Reactants} \rightarrow \text{Products}$$
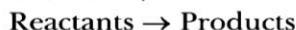
The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$.

$\Delta_r H$ = (sum of enthalpies of products) – (sum of enthalpies of reactants)

$$\sum_i a i\, H_p - \sum_i b i\, H_R$$

Where *ai* and *bi* are the stoichiometric coefficients of products and reactants respectively in a balanced chemical equation.

   (*a*) **Standard Enthalpy of Reaction:** The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its pure form at 1 bar.

   Standard conditions are denoted by adding the superscript 0 to the symbol ΔH, *e.g.*, ΔH^0.

(b) **Enthalpy Changes during Phase Transformations:**

(i) The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called **standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{fus}H^0$.**

(ii) Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its **standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{vap}H^0$.**

(iii) **Standard enthalpy of sublimation, $\Delta_{sub}H^0$** is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1 bar).

(c) **Standard Enthalpy of Formation:** The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable aggregation (also known as reference states) is called **Standard Molar Enthalpy of Formation.** Its symbol is $\Delta_f H^0$.

(d) **Thermochemical Equations:** A thermochemical equation is that chemical equation which includes heat change (enthalpy absorbed or evolved) involved during the reaction. A thermochemical equation can be written in two different ways.

(i) By writing the heat change (enthalpy absorbed or evolved) as a term in the equation e.g.,

$$C(s) + H_2O(g) + 130.4 \text{ kJ/mol} \longrightarrow \underbrace{CO(g) + H_2(g)}_{\text{Water gas}}$$
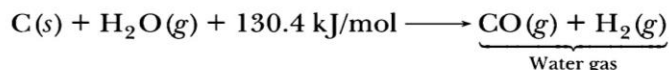
(ii) By using $\Delta_r H^0$ notation i.e., heat evolved or absorbed expressed in terms of $\Delta_r H^0$

$$C(s) + H_2O(g) \longrightarrow \underbrace{CO(g) + H_2(g)}_{\text{Water gas}} \qquad \Delta_r H^0 = +130.4 \text{ kJ/mol}$$
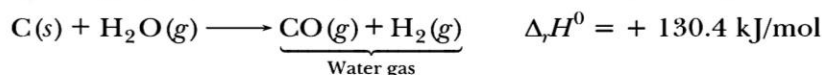
Conventions for Writing Thermochemical Equations

(i) Heat evolved or absorbed during the reaction should be written. For exothermic reactions, ΔH is negative and for endothermic reaction, ΔH is positive.

(ii) The coefficients of different substances represent the number of moles of reactants and products involved in the reaction. $\Delta_r H^0$ value correspond to these coefficients. Thus, the coefficients in a thermochemical equation, if multiplied or divided by some factor, $\Delta_r H^0$ value must also be multiplied or divided by the same factor. For example,

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta_r H^0 = -241.8 \text{ kJ/mol}$$
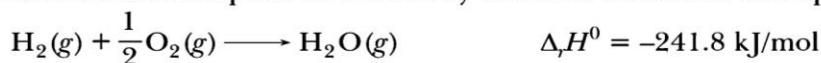
If coefficients are multiplied by 2, the equation takes the form

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g) \qquad \Delta_r H^0 = -483.6 \text{ kJ/mol}$$
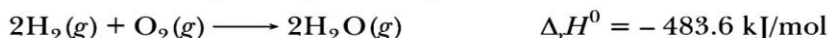
(iii) Unless specified in a given reaction, the value corresponds to the standard states of substances (i.e., enthalpy measured at 298K and 1 atmospheric pressure).

(iv) The physical states (solid, liquid or gas) of different substances must be indicated as the heat evolved or absorbed varies with physical state. For example,

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta_r H^0 = -241.8 \text{ kJ/mol}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta_r H^0 = -285.8 \text{ kJ/mol}$$
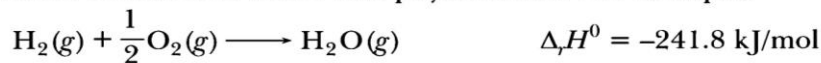
(v) When the chemical equation is reversed, the sign of value is also reversed. However, its magnitude remains the same. For example,

$$H_2(g) + I_2(g) \longrightarrow 2HI(g) \qquad \Delta_r H^0 = +51.9 \text{ kJ/mol}$$

and $\quad 2HI(g) \longrightarrow H_2(g) + I_2(g) \qquad \Delta_r H^0 = -51.9 \text{ kj/mol}$
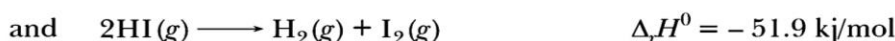
14. **Hess's Law of Constant Heat Summation:** The law states that "*the total amount of heat absorbed or evolved in a physical process or a chemical reaction is same whether the reaction takes place in one step or in a number of steps.* For example, a substance A is converted to substance D in two different ways.

(*i*) A is converted directly to D in one step and the heat evolved is $\Delta_r H$ kJ mol^{-1} *i.e.*,

$$A \longrightarrow D + \Delta_r H \text{ kJ mol}^{-1}$$
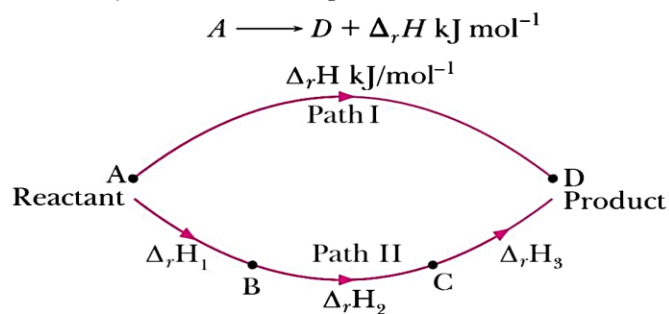
Illustration of Hess's law

(*ii*) A changes to D in three steps involving B and C as intermediate compounds.

$$A \longrightarrow B + \Delta_r H_1 \text{ kJ mol}^{-1}$$

$$B \longrightarrow C + \Delta_r H_2 \text{ kJ mol}^{-1}$$

$$C \longrightarrow D + \Delta_r H_3 \text{ kJ mol}^{-1}$$
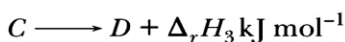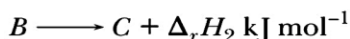
If the ethalpy change during the three respective steps is $\Delta_r H_1, \Delta_r H_2$ and $\Delta_r H_3$ as shown above, then according to Hess's law, the total heat evolved is equal to algebraic sum of enthalpies involved in various steps *i.e.*,

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$$

Thus, Hess's law suggests that the change in heat contents of a chemical reaction depends only on the heat contents of the initial reactants and the final products and independent of the path by which the change has been brought about.

15. **Enthalpies For Different Types of Reactions**

(*a*) **Standard Enthalpy of Combustion ($\Delta_c H^0$):** The amount of heat change when one mole of the substance (compound or element) is completely burnt or oxidised in presence of excess of oxygen. Combustion is always an exothermic process and thus the heat change *i.e.* $\Delta_c H^0$ is always negative.

(*b*) **Enthalpy of Atomization ($\Delta_a H^0$):** It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In case of diatomic molecules, like dihydrogen, the enthalpy of atomization is also the bond dissociation enthalpy.

(*c*) **Bond Enthalpy ($\Delta_{bond} H^0$):** The average bond dissociation energy required to break each bond in a compound is called bond energy.

With reference to the enthalpy changes associated with chemical bonds, two different terms are used:

(*i*) **Bond dissociation enthalpy:** It is defined as the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

(*ii*) **Mean bond enthalpy:** For a polyatomic molecules, the average enthalpy change for breaking one mole bonds of particular type into gaseous molecules is known as mean bond enthalpy.

The bond energies can be used for determining enthalpy change of reactions as
$\Delta_r H^0$ = Sum of bond energies of reactants – Sum of bond energies of products.

of solvent so that further dilution does not give any further heat change. Water is normally used as solvent and the symbol aqueous (*aq*) is used to represent large volume of water, *i.e.*, infinite dilution.

(*f*) **Enthalpy of Dilution($\Delta_{dil}H^0$):** It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

16. **Spontaneity:** A spontaneous process is an irreversible process and may only be reversed by some external agency.

The spontaneous process may be of two types:
(*i*) Spontaneous process in which no initiation is needed. *e.g.*, dissolution of sugar in water.
(*ii*) Spontaneous process where some initiation is required. *e.g.*, in domestic oven, coal keeps on burning once initiated.

(*a*) **Decrease in Enthalpy as a Criterion for Spontaneity:** A chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. Some reactions though endothermic, are spontaneous. Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.

(*b*) **Entropy and Spontaneity:** Entropy is a measure of degree of randomness or disorder in an isolated system. It is a state function and is represented by the symbol '*S*'.

It was concluded that any such process in which the total randomness of the universe (system + surrounding) increases is a spontaneous process.

(*i*) For a reversible process,

$$\Delta S_{system} = \frac{+q_{sys,\,rev}}{T}$$

$$\Delta S_{surroundings} = -\frac{q_{surrounding,\,rev}}{T}$$

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings} = 0 \text{ (at equilibrium)}$$

In case of adiabatic reversible process, $q = 0$

$\therefore \quad \Delta S_{Total} = 0$

(*ii*) For irreversible process, $\Delta S_{Total} > 0$. Thus, entropy of the universe increases (for a spontaneous change).

(*c*) **Entropy and Second Law of Thermodynamics:** Some common definitions of the second law of thermodynamics are given below:

"All spontaneous processes are thermodynamically irreversible."

OR

"It is impossible to convert heat completely into equivalent amount of work without producing changes elsewhere."

OR

"Whenever a spontaneous process occurs, it is accompanied by an increase in the total entropy of the universe."

OR

"Heat cannot by itself pass from a colder to a hotter body without the use of an external agency."

(*d*) **Gibbs Energy and Spontaneity:** A thermodynamic function, the Gibbs energy or Gibbs function, *G*, is expressed as

$$G = H - TS$$

Gibbs function, *G* is an extensive property and a state function.

The free energy change (ΔG) is the true criterion for determining the spontaneity of a process.

The resultant driving force, $\Delta H - T\Delta S$, is related to free energy in the form of **Gibbs- Helmholtz equation**

$$\Delta G = \Delta H - T\Delta S$$

ΔG is the free energy change which is actually the measure of the useful work available from a chemical reaction.

It is thus the free energy change which determines the spontaneity of a reaction. For a change to be spontaneous, ΔG must be negative.

Table 2.1: Effect of ΔH and $T\Delta S$ on Spontaneity

ΔH	ΔS	$\Delta G = H - T\Delta S$	Inference
–ve	+ve	–ve	Process is spontaneous at all temperatures.
+ve	–ve	+ve	Process is non-spontaneous at all temperatures.
–ve	–ve	–ve at low T	Process is spontaneous only at low temperatures.
–ve	–ve	+ve at high T	Process is non-spontaneous at high temperatures.
+ve	+ve	+ve at low T	Process is non-spontaneous at low temperatures.
+ve	+ve	–ve at high T	Process is spontaneous at high temperatures.

(e) **Absolute Entropy and Third Law of Thermodynamics:** The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called **third law of thermodynamics.**

17. **Gibbs Energy Change and Equilibrium**

At equilibrium

$$\Delta_r G = 0$$

Gibbs energy for a reaction in which all reactants and products are in standard state. $\Delta_r G°$ is related to the equilibrium constant of the reaction as follows:

$$\Delta_r G° = -RT \ln K$$

or $\quad \Delta_r G° = -2.303\, RT \log K$

We also know that

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -RT \ln K .$$

IMPORTANT FORMULAE

1. **First law of thermodynamics: $\Delta U = q + w$**

Where, ΔU is change in internal energy q is heat and w is work done on the system.

2. **Relationship between change in enthalpy (ΔH) and change in internal energy ΔU:**

$$\Delta H = \Delta U + p.\Delta V$$

p is pressure and ΔV is change in volume.

or, $\Delta H = \Delta U + \Delta n RT$

$\Delta n = n_{\text{gaseous products}} - n_{\text{gaseous reactants}}$

R = Gas constant

T = Temperature

3. **Enthalpy change ΔH in terms of bond energy:**

$$\Delta H_{\text{reaction}} = \Sigma \text{bond enthalpies reactants} - \Sigma \text{bond enthalpies products}$$

4. **Enthalpy change ΔH in terms of heat of formation:**

$$\Delta H°_{\text{reaction}} = \Sigma H°_{f(\text{Products})} - \Sigma H°_{f(\text{reactants})}$$

5. **Hess's law of constant Heat summation**

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

6. **Relationship between Gibbs energy change and Equilibrium constant:**

$$\Delta_r G° = \Delta_r H° - T \Delta_r S° = - RT \ln K$$

where $\Delta_r G°$ = Gibbs energy change for reaction

$\Delta_r H°$ = Enthalpy change of reaction

$\Delta_r S°$ = Entropy change of reaction

R = Gas constant, K = Equilibrium constant, T = Temperature

NCERT TEXTBOOK QUESTIONS

1. **Choose the correct answer. A thermodynamic state function is a quantity**
   - (i) **used to determine heat changes.**
   - (ii) **whose value is independent of path.**
   - (iii) **used to determine pressure volume work.**
   - (iv) **whose value depends on temperature only.**

Ans. (ii), A thermodynamic state function is a quantity whose value is independent of path.

2. **For the process to occur under adiabatic conditions, the correct condition is**
   - (i) $\Delta T = 0$
   - (ii) $\Delta p = 0$
   - (iii) $\Delta q = 0$
   - (iv) $w = 0$

Ans. (iii), $\Delta q = 0$

3. **The enthalpies of all elements in their standard states are**
   - (i) **unity**
   - (ii) **zero**
   - (iii) **< 0**
   - (iv) **different for each element**

Ans. (ii), zero

4. **$\Delta U°$ of combustion of methane is $-X$ kJ mol^{-1}. The value of $\Delta H°$ is**
   - (i) $= \Delta U°$
   - (ii) $> \Delta U°$
   - (iii) $< \Delta U°$
   - (iv) $= 0$

Ans. (iii), $< \Delta U°$

5. **The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are $- 890.3$ kJ mol^{-1}, $- 393.5$ kJ mol^{-1} and $- 285.8$ kJ mol^{-1} respectively. Enthalpy of formation of $CH_4(g)$ will be**
   - (i) $- 74.8$ kJ mol^{-1}
   - (ii) $- 52.27$ kJ mol^{-1}
   - (iii) $+74.8$ kJ mol^{-1}
   - (iv) $+52.26$ kJ mol^{-1}

Ans. (i), $- 74.8$ kJ mol^{-1}

6. **A reaction $A + B \longrightarrow C + D + q$ is found to have a positive entropy change. The reaction will be**
   - (i) **possible at high temperature.**
   - (ii) **possible only at low temperature.**
   - (iii) **not possible at any temperature.**
   - (iv) **possible at any temperature.**

Ans. (iv), possible at any temperature

7. **In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy of the process?**

Ans. In the given case,

$$q = 701 \text{ J}, w = - 394 \text{ J}$$

According to the first law of thermodynamics,

$$\Delta U = q + w = + 701 + (- 394) = + 307 \text{ J}$$

Thus, internal energy increases by **307 J**

8. **The reaction of cynamide. $NH_2CN(s)$, with dioxygen was carried out in a bomb calorimeter and ΔU was found to be -742.7 kJ mol^{-1} at 298 K. Calculate enthalpy change for the reaction at 298 K.**

$$NH_2CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(l);$$
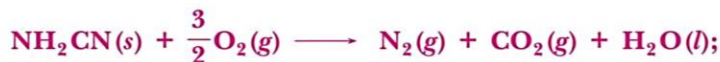
Ans. For the given reaction,

$$\Delta n_g = (1+1) - \left(\frac{3}{2}\right) = +\left(\frac{1}{2}\right) \text{mol.}$$

$$\Delta H = \Delta U + \Delta n_g RT$$

we have, $\Delta H = -742.7 + (\frac{1}{2} \times 8.314 \times 10^{-3} \times 298)$ $(\because R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})$

$$= -741.5 \text{ kJ mol}^{-1}$$

9. **Enthalpy of combustion of carbon to CO_2 is – 393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.**

Ans. The corresponding equation is

$$C(s) + O_2(g) \rightarrow \underset{\text{1 mole = 44 g}}{CO_2(g)} ; \Delta H = -393.5 \text{ kJ/mol}$$
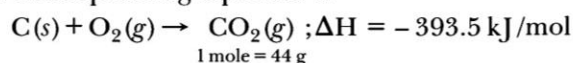
Heat released during the formation of 44 g of CO_2
$$= -393.5 \text{ kJ}$$
Heat released upon formation of 35.2 g of CO_2

$$= -\frac{393.5}{44} \times 35.2 = -314.8 \text{ kJ/mol}$$

∴ The value of ΔH involved in the formation of 35.2 g of CO_2
$$= -314.8 \text{ kJ}$$

10. **Enthalpies of formation of $CO(g)$, $CO_2(g)$, $N_2O(g)$ and $N_2O_4(g)$ are – 110, – 393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:**

$$N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$$

Ans. $\Delta_r H = \Sigma\Delta_f H(\text{products}) - \Sigma\Delta_f H (\text{reactants})$

$$= \{\Delta_f H [N_2O(g)] + 3 \times \Delta_f H[CO_2(g)]\} - \{\Delta_f H [N_2O_4(g)] + 3 \times \Delta_f H[CO(g)]\}$$

$$= \{81 + [3 \times (-393)]\} - \{9.7 + 3 \times (-110)\} \text{ kJ/mol}$$

$$= (-1098) - (-320.3) \text{ kJ/mol}$$

$$= -777.7 \text{ kJ/mol}$$

11. **Given $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta_r H° = -92.4$ kJ mol^{-1}. What is the standard enthalpy of formation of NH_3 gas?**

Ans. Reaction corresponding to the formation of ammonia can be written as

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$$
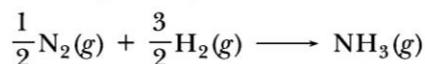
∴ $\Delta_f H°[NH_3(g)] = \frac{1}{2}\Delta_r H°$

$$= \frac{1}{2} \times (-92.4) = -46.2 \text{ kJ mol}^{-1}$$

12. **Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data:**

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \Delta_r H° = -726 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g); \Delta_c H° = -393 \text{ kJ mol}^{-1}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \Delta_f H° = -286 \text{ kJ mol}^{-1}$$
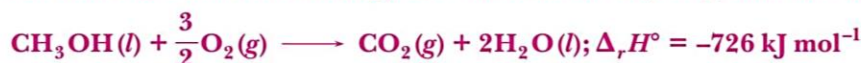
Ans. In the given data,

$$\Delta_c H°[CO_2(g)] = \Delta_f H°[CO_2(g)] = -393 \text{ kJ mol}^{-1}$$

$$\therefore \quad \Delta_r H° = \Sigma\Delta_f H°(\text{products}) - \Sigma\Delta_f H°(\text{reactants})$$

or $\Delta_r H° = \{\Delta_f H°[CO_2(g)] + 2\times\Delta_f H°[H_2O(l)]\} - \{\Delta H°_f[CH_3OH(l) + \dfrac{3}{2}\times\Delta_f H°[O_2(g)]\}$

or $-726 = \{-393 + 2\times(-286)\} - \{\Delta_f H°[CH_3OH(l)] + \dfrac{3}{2}\times 0\}$

or $-726 = \{-965) - \Delta_f H°[CH_3OH(l)]$

or $\Delta_f H°[CH_3OH(l)] = +726 - 965 = \mathbf{-239 \text{ kJ mol}^{-1}}$

13. **Calculate enthalpy change for the process**

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$
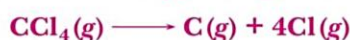
and calculate bond enthalpy of C—Cl in $CCl_4(g)$.

$$\Delta_{vap} H°[CCl_4] = 30.5 \text{ kJ mol}^{-1}$$

$$\Delta_f H°[CCl_4] = -135.5 \text{ kJ mol}^{-1}$$

$$\Delta_a H°[C] = 715.0 \text{ kJ mol}^{-1}$$

$$\Delta_a H°[Cl_2] = 242 \text{ kJ mol}^{-1}$$

where $\Delta_a H°$ is enthalpy of atomisation.

Ans. The given data can be expressed as follows.

$$CCl_4(l) \longrightarrow CCl_4(g); \Delta_{vap}H° = 30.5 \text{ kJ mol}^{-1} \qquad \ldots(i)$$

$$C(s) + 2Cl_2(g) \longrightarrow CCl_4(l); \Delta_f H° = -135.5 \text{ kJ mol}^{-1} \qquad \ldots(ii)$$

$$C(s) \longrightarrow C(g); \Delta_a H° = 715.0 \text{ kJ mol}^{-1} \qquad \ldots(iii)$$

$$Cl_2(g) \longrightarrow 2Cl(g); \Delta_a H° = 242 \text{ kJ mol}^{-1} \qquad \ldots(iv)$$
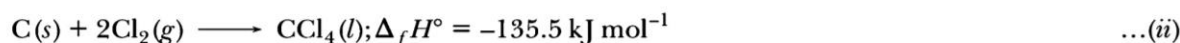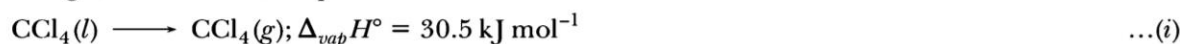
The required equation is

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$
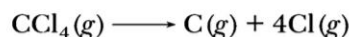
The required equation can be obtained as follows:

Equation (iii) + 2 × Equation (iv) – Equation (i) – Equation (ii)

Thus, we have

$$\Delta H = [715.0 + (2\times 242) - 30.5 - (-135.5)]\text{kJ/mol}$$

or $CCl_4(g) \longrightarrow C(g) + 4Cl(g); \Delta H = 1304 \text{ kJ mol}^{-1}$
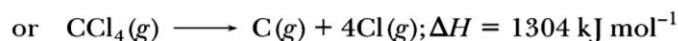
Hence, the enthalpy change for the given process is 1304 kJ mol^{-1}.

Bond enthalpy of C—Cl in $CCl_4(g)$

$$= \frac{1304}{4} = \mathbf{326 \text{ kJ mol}^{-1}}$$

14. **For an isolated system, $\Delta U = 0$, what will be ΔS?**

Ans. For an isolated system, $\Delta U = 0$ and for a process to be spontaneous, the value of ΔS must be positive.

15. **For the reaction at 298 K,**

$$2A + B \longrightarrow C,$$
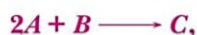
$\Delta H = 400 \text{ kJ mol}^{-1}$ and $\Delta S = 0.2 \text{ kJ/K/ mol.}$

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range?

Ans. When $\Delta G = 0$, the reaction will be at equilibrium.

The temperature at which the reaction is in equilibrium can be obtained as follows

$\because \qquad \Delta G = \Delta H - T\Delta S$

or $\qquad T = \dfrac{\Delta H - \Delta G}{\Delta S} = \dfrac{400 - 0}{0.2} = \textbf{2000 K}$

The reaction will be spontaneous when ΔG is negative. This is possible only at a temperature greater than 2000 K.

16. For the reaction, $2Cl(g) \longrightarrow Cl_2(g)$, what are the signs of ΔH and ΔS?

Ans. The given reaction involves the formation of Cl—Cl bond. The process will therefore involve a release of energy, *i.e.*, ΔH will be negative. Further, the process involves a decrease in the randomness because 2 moles of isolated atoms will have greater randomness than one mole of a molecule. Hence, entropy decreases, *i.e.*, ΔS is negative. Thus, in the given process both ΔH and ΔS are negative.

17. For the reaction $2A(g) + B(g) \longrightarrow 2D(g)$; $\Delta U^\circ = -10.5$ kJ and $\Delta S^\circ = -44.1$ JK^{-1}

Calculate ΔG° for the reaction, and predict whether the reaction may occur spontaneously.

Ans. For the given reaction, $\Delta n_g = 2 - (2 + 1) = -1$

$\therefore \quad \Delta H^\circ = \Delta U^\circ + \Delta n_g RT$

$\qquad = -10.5 + (-1) \times 8.314 \times 10^{-3}$ kJ mol^{-1} K$^{-1} \times 298$ ($\because R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1} and all substances are in standard states, *i.e.*, $T = 298$ K).

$\qquad = -12.98$ kJ

Hence, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\qquad = -12.98 - [298 \times (-44.1 \times 10^{-3})]$

$\qquad = \textbf{0.162 kJ}$

Since, ΔG° for the process is positive, the reaction will not occur spontaneously.

18. The equilibrium constant for a reaction is 10. What will be the value of ΔG°? $R = 8.314$ JK^{-1} mol^{-1}, $T = 300$ K.

Ans. $\because \qquad \Delta G^\circ = -2.303$ RT $\log_{10}$K

we have $\Delta G^\circ = -2.303 \times 8.314 \times 300 \times \log_{10}10$

$\qquad = -2.303 \times 8.314 \times 300 \times 1 = -5744.1$ J/mol

$\qquad = \textbf{-5.744 kJ/mol}$

19. Comment on the thermodynamic stability of NO$_2(g)$, given

$\dfrac{1}{2}N_2(g) + \dfrac{1}{2}O_2(g) \rightarrow NO(g)$; $\Delta_r H^\circ = 90$ kJ mol^{-1}

$NO(g) + \dfrac{1}{2}O_2(g) \rightarrow NO_2(g)$; $\Delta_r H^\circ = -74$ kJ mol^{-1}
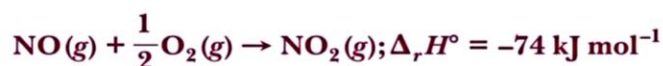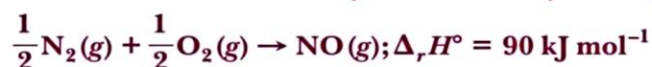
Ans. In the formation of NO(g), heat is absorbed. Therefore, NO(g) has a higher heat energy than the reactants and therefore is unstable. On the other hand, formation of NO$_2(g)$ involves release of heat energy. Hence, NO$_2(g)$ has a lower heat energy and is stable. Thus, unstable NO(g) changes to stable NO$_2(g)$.

20. Calculate the entropy change in surroundings when 1.00 mol of H$_2$O(*l*) is formed under standard conditions.

[Given: $\Delta_f H^\circ = -286$ kJ mol^{-1}]

Ans. The standard enthalpy of formation of H$_2$O (*l*), *i.e.*, $\Delta_f H^\circ$ is -286 kJ mol^{-1}. It implies that

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formation of $H_2O(l)$ is an exothermic process and 286 kJ mol^{-1} heat is evolved. This heat is absorbed by the surroundings. Thus,

$$q_{surr} = +286 \text{ kJ mol}^{-1}$$

Hence, entropy change in surroundings is

$$\Delta S_{surr} = \frac{q_{surr}}{T} = \frac{286}{298} = 0.9597 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$= \textbf{959.7 JK}^{-1} \textbf{ mol}^{-1}$$

CASE-BASED QUESTIONS

1. **The study of energy transformations forms the subject matter of thermodynamics.**

   Most of the reactions fall into the category of either closed systems or open systems. For these systems, neither decrease in enthalpy (ΔH) nor increase in entropy (ΔS) can determine the direction of spontaneous change. Gibb's free energy (ΔG) combines these two factors in one equation as $\Delta G = \Delta H - T\Delta S$.

   ΔH_f and $S°$ values for N_2, H_2 and NH_3 are given below:

	ΔH_f (kJ/mol)	$S°$ (JK^{-1}mol^{-1})
$N_2(g)$	0	192
$H_2(g)$	0	131
$NH_3(g)$	−46	193

   Based on the above information, answer the following questions:

   (i) Calculate $\Delta H°_f$ for the reaction:

   $$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

   (ii) Under what conditions, the system will never be spontaneous?

   (iii) Give mathematical relation between free energy change and equilibrium constant.

   (iv) Define spontaneous process.

   (v) Which quantity out of $\Delta_r G = \Delta_r G°$ will be zero at equilibrium?

   Answers

   (i) $\Delta H°_f = 2 \Delta H°_f (NH_3) - \Delta H°_f (N_2) - 3\Delta H°_f (H_2)$
   $= 2 \times (-46) - 0 - (3 \times 0) = -92$ kJ/mol
   $= -92,000$ J/mol

   (ii) As $\Delta G = \Delta H - T \Delta S$

   When ΔH is + ve and ΔS is −ve, then ΔG will also become +ve irrespective of the values. As ΔG will be +ve, so the system will never be spontaneous.

   (iii) $\Delta G° = -RT \ln k$

   (iv) A spontaneous process is an irreversible process and may only be reversed by some external agency.

   (v) $\Delta_r G$ will be always be zero at equilibrium whereas $\Delta_r G°$ will be zero only if $k = 1$.

2. **Thermodynamic System:**

   A thermodynamic system, delimited from the surroundings by real or hypothetical boundaries, can either be (1) isolated, (2) adiabatic, (3) closed, or (4) open, depending on the type of exchange between the system under consideration and the surroundings. A system is defined as isolated in the absence of any exchange of energy or matter with the surroundings, adiabatic if only work is exchanged, closed if only energy is exchanged, and open if both energy and matter can be exchanged.

The state of a thermodynamic system is defined by its internal energy, U, and entropy, S, as well as a set of state variables, including temperature T, hydrostatic pressure p, volume V, and number of moles of components n. The former two thermodynamic quantities are functions of the state variables. Among these, temperature and pressure constitute intensive variables, which define properties independent of the size of the system, whereas volume, internal energy, and entropy constitute extensive variables, values of which vary with the size of the system. Intensive molar properties are obtained by dividing extensive properties by the number of moles n. The molar volume V_m is defined, for instance, by $V_m = V/n$. It is important to point out that the aforementioned state functions depend on the conditions, or in other words, the state of the system, but not on the path, process, or history that was followed to reach it.

[**Source:** Anna L. Smith, Rudy J.M. Konings, in Advances in Nuclear Fuel Chemistry, 2020]

Based on the above information, answer the following questions:

(*i*) **What do you understand by terms system and surroundings?**

(*ii*) **Why do all living systems considered as open system?**

(*iii*) **What do you understand by the term thermodynamic equilibrium?**

(*iv*) **What type of systems does the following examples represents?**

    (*a*) **Hot tea placed in a cup.**

    (*b*) **Hot tea placed in a sealed metallic tea pot.**

(*v*) **Which one of the following is not an extensive state function?**

    Enthalpy change, Internal energy and Pressure.

Answers

(*i*) A system may be defined as that specific part of the universe which is under study and possesses fixed boundaries. The boundaries may be real or imaginary. The rest of the universe is referred to as surroundings.

(*ii*) All living systems are open systems because they continuously exchange matter and energy with the surroundings.

(*iii*) A system is said to be in thermodynamic equilibrium if its macroscopic properties like temperature, pressure etc. do not change with time.

(*iv*) (*a*) Open system

    (*b*) Closed system

(*v*) Pressure is an intensive state function.

SHORT ANSWER QUESTIONS–I (2 marks)

1. **Why mole fraction is an intensive property?**

Ans. In general, ratio of two extensive property is always intensive, *i.e.*

$$\frac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$$

As moles of component is an extensive property and, total no. of moles is also extensive.

Therefore, mole fraction $= \dfrac{\text{Moles of components}}{\text{Total no. of moles}}$

$$= \frac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$$

2. **Differentiate between reversible and irreversible process.**

Ans.

Reversible process	Irreversible process
(i) The process is carried out infinitesimally slowly in such a way that each step remains in equilibrium with the previous step and the process can be reversed at any stage.	(i) The process is carried out in a single step to transit the system from the initial state to the final state.
(ii) This is completely imaginary.	(ii) This process actually occur in nature.
(iii) It takes infinite time for completion.	(iii) It takes finite time for completion.

3. **Assign proper sign to q and w in the following cases:**

   (i) A system transfers 10 kJ of energy to the surroundings.

   (ii) Surroundings transfer 25 kJ of energy to the system.

   (iii) 15 kJ of energy is transferred to the system by doing work on it.

   (iv) 30 kJ of energy is lost by the system on account of the work done by the system on the surroundings.

Ans.   (i) $q = -10$ kJ   (ii) $q = +25$ kJ

(iii) $w = +15$ kJ   (iv) $w = -30$ kJ

4. **Identify the state functions and path functions out of the following: enthalpy, entropy, heat, temperature, work, free energy?**   [*NCERT Exemplar*]

Ans.   **State function:** Temperature, Enthalpy, Entropy, Free energy

Path function: Work, Heat.

5. **(i) Write an expression for work done in an isothermal and irreversible expansion of a gas.**

   (ii) What do mean by the term free expansion?

Ans.   (i) $w_{irrev} = -p_{ex} \int\limits_{V_1}^{V_2} dV$

or $\boxed{w_{irrev} = -p_{ex}(V_2 - V_1)}$

where, p_{ex} is the external pressure of the gas, V_1 is the initial volume of the gas and V_2 is the final volume of the gas.

(ii) Expansion of a gas in vacuum (*i.e.*, external pressure, $p_{ex} = 0$) is called free expansion. The free expansion of an ideal gas does not involve any work whether the process is reversible or irreversible.

6. **Comment on the statement: Heat is a random form of energy but work is an organised form of energy.**

Ans.   Heat is a form of energy transfer associated with random motion of the microscopic particles while work is the organised form of energy transfer associated with the motion of microscopic particles as a whole in a certain direction.

7. **(i) What is the main limitation of the first law of thermodynamics?**

   (ii) What will happen to internal energy if work is done on the system?

Ans.   (i)   First law of thermodynamics fails to predict the spontaneity of a process.

(ii) The internal energy of the system will increase if work is done on the system.

8. **Calculate the calorific value of methane if it burns according to the equation.**

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \Delta_c H^0 = -890.0 \text{ kJ}$$
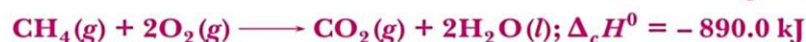
Ans.   According to the given equation, one mole (16 g) of CH_4 produce heat equal to –890 kJ.

∴   Heat produced per gram $= -\dfrac{890.0}{16} = -55.6$ kJ/g

or $= 13.28$ kcal/g

9. **18.0 g of water completely vapourises at 100°C and 1 bar pressure and the enthalpy change in the process is 40.79 kJ mol⁻¹. What will be the enthalpy change for vapourising two moles of water under the same conditions? What is the standard enthalpy of vapourisation for water?**
   [NCERT Exemplar]

Ans. 18 g of H_2O = 1 mol H_2O

Given that the enthalpy change for 1 mole of water = 40.79 kJ/mol. Therefore, enthalpy change for 2 moles of water = 2 × 40.79 = **+ 81.58 kJ**

The standard enthalpy of vapourisation at 100°C and 1 bar pressure;

$$\Delta_{vap}H = \mathbf{+\ 40.79\ kJ/mol}$$

10. **One mole of acetone requires less heat to vapourise than 1 mol of water. Which of the two liquids has higher enthalpy of vapourisation?** *[NCERT Exemplar]*

Ans. Due to weak force of attraction between molecules, acetone requires less heat to vapourise. Therefore water has higher enthalpy of vapourisation.

11. **Standard molar enthalpy of formation, $\Delta_f H°$ is just a special case of enthalpy of reaction, $\Delta_r H°$. Is the $\Delta_r H°$ for the following reaction same as $\Delta_f H°$? Give reason for your answer.**

$$\mathbf{CaO\,(s) + CO_2\,(g) \longrightarrow CaCO_3\,(s); \Delta_f H° = -178.3\ kJ\ mol^{-1}}$$ *[NCERT Exemplar]*
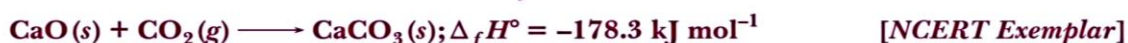
Ans. In the above equation, enthalpy of formation and enthalpy of reaction is not same. This is because here calcium carbonate is getting formed from other compounds and not from its constituent elements.

12. **The value of $\Delta_f H°$ for NH_3 is –91.8 kJ mol⁻¹. Calculate enthalpy change for the following reaction:**

$$\mathbf{2NH_3(g) \rightarrow N_2(g) + 3H_2(g)}$$ *[NCERT Exemplar]*

Ans. Given, $\dfrac{1}{2}N_2\,(g) + \dfrac{3}{2}H_2\,(g) \longrightarrow NH_3\,(g); \Delta_f H° = -91.8\,kJ/mol$

For the reaction; $2NH_3\,(g) \longrightarrow N_2\,(g) + 3H_2\,(g)$
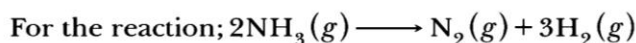
The enthalpy change will be **+ 183.6 kJ/mol**

13. **The enthalpy of atomisation for the reaction $CH_4(g) \rightarrow C(g) + 4H(g)$ is 1665 kJ mol⁻¹. What is the bond energy of C–H bond?** *[NCERT Exemplar]*

Ans. $CH_4(g) \rightarrow C(g) + 4H(g); \Delta_a H° = 1665\ kJ\ mol^{-1}$

Since, Enthalpy of atomisation of 4 moles of C—H bonds = 1665 kJ mol⁻¹

∴ C—H bond energy, per mole $= \dfrac{1665}{4}kJ\ mol^{-1} = \mathbf{416.2\ kJ\ mol^{-1}}$

14. (i) **Given that $\Delta H = 0$ for mixing of two gases. Explain whether the diffusion of these gases into each other in a closed container is a spontaneous process or not?**

   (ii) **Heat has randomising influence on a system and temperature is the measure of average chaotic motion of particles in the system. Write the mathematical relation which relates these three parameters.** *[NCERT Exemplar] [HOTS]*

Ans. (i) The diffusion will be a spontaneous process. The greater the disorder in an isolated system, the higher is the entropy. Therefore, the process will be spontaneous.

   (ii) Entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as:

$$\Delta S = \dfrac{q_{rev}}{T}$$

15. **Increase in enthalpy of the surroundings is equal to decrease in enthalpy of the system. Will the temperature of system and surroundings be the same when they are in thermal equilibrium?**
   [NCERT Exemplar]

Ans. If the system is in thermal equilibrium with the surroundings, then the temperature of the surroundings will be same as that of the system. Also increase in enthalpy of the surroundings is equal to decrease in the enthalpy of the system.

16. At 298 K, K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.98. Predict whether the reaction is spontaneous or not. **[NCERT Exemplar]**

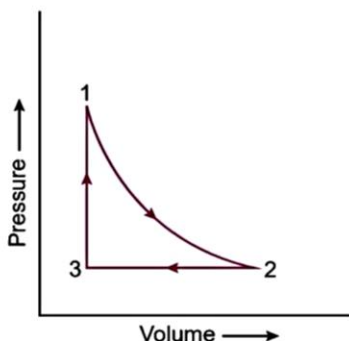**Ans.** $\Delta_t G° = \Delta_r H° - T\Delta_r S° = - RT \ln K$

For the process to be spontaneous ΔG should be negative.

Since, $K_p = 0.98$; $i.e$, $K_p < 1$

$\therefore \quad \Delta_r G°$ is + ve

Hence, the reaction will be non-spontaneous.

17. A sample of 1.0 mol of a monoatomic ideal gas is taken through a cyclic process of expansion and compression as shown figure given below. What will be the value of ΔH for the cycle as a whole? **[NCERT Exemplar]**

Ans. Enthalpy change for a cyclic process is $\Delta H = 0$. This is because enthalpy change is a state function.

18. The standard molar entropy of $H_2O(l)$ is 70 $JK^{-1} mol^{-1}$. Will the standard molar entropy of $H_2O(s)$ be more, or less than 70 $JK^{-1} mol^{-1}$. **[NCERT Exemplar]**

Ans. Standard molar entropy of $H_2O(s)$ will be less than 70 J/K/mol because ice is the more ordered form of water and thus, the entropy will decrease.

19. (i) The molar enthalpy of vapourisation of acetone is less than that of water. Why?

(ii) Predict the change in internal energy for an isolated system at constant volume.

[NCERT Exemplar]

Ans. (i) Due to strong intermolecular force of attraction (hydrogen bonding) in water molecules, it has high enthalpy of vapourization than acetone.

(ii) If there is no transfer of energy as heat or as work (an isolated system)

$i.e.$, if $w = 0$ and $q = 0$, then $\Delta U = 0$.

20. Expansion of a gas in vaccum is called free expansion. Calculate the work done and the change in internal energy when 1 litre of ideal gas expands isothermally into vaccum until its total volume is 5 litre? **[NCERT Exemplar]**

Ans. Expansion of a gas in vacuum ($p_{ext} = 0$) is called free expansion.

Now $w = -p_{ext}(V_2 - V_1)$

As $p_{ext} = 0$

$\therefore \quad w = -0(5 - 1)$

$\Rightarrow \quad w = 0$

For isothermal expansion, $q = 0$

By first law of thermodynamics

$q = \Delta U + (-w)$

$\Rightarrow \quad 0 = \Delta U + 0$

So, $\Delta U = 0$

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21. If the combustion of 1 g of graphite produces 20.7 kJ of heat, what will be molar enthalpy change? Give the significance of sign also. [*NCERT Exemplar*]

Ans. Molar enthalpy change of graphite = enthalpy change for 1 g carbon × molar mass of carbon

$$= -20.7 \text{ kJ g}^{-1} \times 12 \text{ g mol}^{-1}$$

$$\Delta H = -2.48 \times 10^2 \text{ kJ mol}^{-1}$$

The negative sign of ΔH indicates that the reaction is exothermic.

22. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in reactant molecules minus amount of energy required to form all the bonds in the product molecules. What will be the enthalpy change for the following reaction?

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$
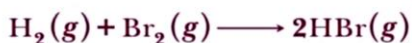
Given that Bond energy of H_2, Br_2 and HBr is 435 kJ mol^{-1}, 192 kJ mol^{-1} and 368 kJ mol^{-1} respectively. [*NCERT Exemplar*]

Ans. $\Delta_r H° = \Sigma bond\ enthalpies_{reactants} = - \Sigma bond\ enthalpies_{products}$

$\Delta_r H° = bond\ energy\ of\ H_2 + Bond\ energy\ of\ Br_2 - 2 \times 2\ Bond\ energy\ of\ HBr$

$$= 435 + 192 - (2 \times 368) \text{ kJ mol}^{-1}$$

$$\Delta_r H° = -109 \text{KJ mol}^{-1}$$

23. The enthalpy of vapourisation of CCl_4 is 30.5kJ mol^{-1}. Calculate the heat required for the vapourisation of 284 g of CCl_4 at constant pressure. (Molar mass of CCl_4 = 154 g mol^{-1}). [*NCERT Exemplar*]

Ans. Given that enthalpy of vaporization of 1 mole of CCl_4 = 30.5 kJ/mol.

1 mole or 154 g CCl_4 requires heat of vaporization = 30.5 kJ/mol.

∴ Heat required for vapourisation of 284 g of CCl_4

$$= \frac{284 \text{ g}}{154 \text{ g mol}^{-1}} \times 30.5 \text{ kJ/mol} = \textbf{56.2 kJ}$$

24. The enthalpy of reaction for the reaction:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \text{ is } \Delta_r H° = -572 \text{kJ mol}^{-1}$$

What will be standard enthalpy of formation of $H_2O(l)$? [*NCERT Exemplar*]

Ans. The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation is called standard molar enthalpy of formation. Its symbol is $\Delta_f H°$.

According to the definition of standard enthalpy of formation, the enthalpy change for the following reaction will be standard enthalpy of formation of $H_2O(l)$.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$
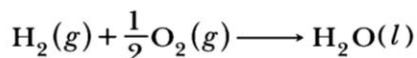
Thus, $\Delta_f H°_{H_2O}(l) = \frac{1}{2} \times \Delta_r H° = \frac{-572 \text{ kJ mol}^{-1}}{2} = \textbf{-286kJ/mol}$

25. Why is heat of neutralisation for a strong acid and strong base constant?

Ans. Heat of neutralisation is the change in enthalpy of the system when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base or vice versa in dilute solution.

For strong acid and strong base the heat of neutralisation is always constant and is equal to − 57.1 kJ (− 13.7 kcal). This can be explained on the basis of Arrhenius theory of electrolytic dissociation. According to this theory, the neutralisation of 1 gm equivalent a strong acid with 1 gm equivalent of a strong base involves the combination of 1 gm equivalent of each H^+ and OH$^-$. This is why the value of heat of neutralisation remains constant for a strong acid and a strong base.

26. **Predict the sign of $\Delta S°$ for the following reactions.**

   (i) $2H_2S(g) + 3O_2(g) \longrightarrow 2H_2O(g) + 2SO_2(g)$

   (ii) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
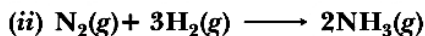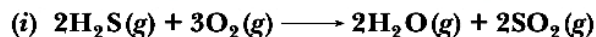
Ans. (i) In the given reaction

   Δn_g = no. of moles of gaseous products – no. of moles of gaseous reactants

   $= 4 - 5 = -1$

   Since, no of moles decreases and therefore randomness decreases i.e. $\Delta S^0 = -$ ve.

   (ii) $\Delta n_g = 2 - 4 = -2$. $\Delta S = -$ ve, because there is decrease in no. of gas molecules.

27. **An ideal gas is allowed to expand against a constant pressure of 2 bar from 10 L to 50 L in one step. Calculate the amount of work done by the gas. If the same expansion were carried out reversibly, will the work done be higher or lower than the earlier case?**

   (Given that 1 L bar = 100 J) [NCERT Exemplar]

Ans. Work done in the process can be calculated as

   $w = -p_{ext}(V_f - V_i) = -2 \times 40 = -80$ L bar = **–8kJ**

   The negative sign shows that work is done by the system on the surroundings. Work done will be more in the reversible expansion because internal pressure is infinitesimally greater than the external pressure.

SHORT ANSWER QUESTIONS–II   (3 marks)

1. **What is pressure-volume work? Derive an expression for the pressure-volume work.**

Ans. **Pressure-volume work:** It is the work done when the gas expands or contracts against the external pressure. It is also called expansion work.

   Derivation of expression for pressure-volume work.

   Let us consider, a gas enclosed in a cylinder fitted with a movable piston as shown in figure. Suppose the volume of the gas in the cylinder is V and the area of cross-section of the piston is A. Suppose, an external pressure, p_{ext} is exerted through the piston and the piston moves a very small distance dl, the change in volume dV in given by

   $dV = A \times dl$

   Since, pressure $= \dfrac{\text{Force}}{\text{Area}}$

   The force acting on the piston will be given by

   Force on piston $= p_{ext} \times A$

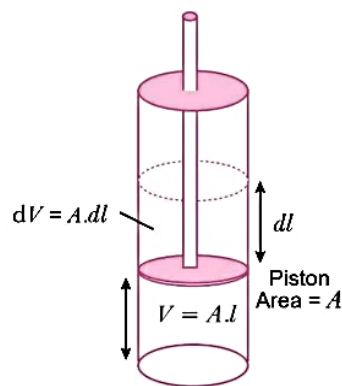   If the work done by small movement of the piston is dw, we have

   $dw = -p_{ext} \times A \times dl$ ($\because A \times dl = dV$)

   $= -p_{ext}\,dV$

   If p_{ext} is constant, the total work done, w is given by

   $w = -\int_{V_1}^{V_2} p_{ext}\,dV = -p_{ext}(V_2 - V_1)$

   $= -p_{ext}\,\Delta V$

   $\boxed{w = -p_{ext}.\Delta V}$

$dV = A.dl$

dl

Piston
Area $= A$

$V = A.l$

2. **Derive an expression for the work done in the isothermal and reversible expansion of an ideal gas.**

Ans. **Work done in isothermal and reversible expansion of an ideal gas**

   Suppose an ideal gas is taken at temperature T in a cylinder which is fitted with a frictionless and weightless piston.

Let the initial volume of the gas be V_1 and the pressure p_1 as shown in figure. Suppose the gas expands reversibly and isothermally from volume V_1 to volume V_2. Due to expansion, the pressure of the gas falls from p_1 to p_2.

Since, the expansion of the gas is reversible, it must be carried out in infinitesimally small steps. Suppose, initially the pressure of the gas p is equal to the external pressure p_1 and piston is stationary. Now p_1 is decreased by one infinitesimally amount dp. The gas undergoes expansion and the piston moves by a distance dl.

Since, dp is very small, we can assume $p_1 = p_{gas} = p$

The work (dw) done by the gas in one infinitesimally step is given by

$$dw = -p \times A \times dl = -p \times dV$$

where, A is the area of cross-section of the piston and dV is the increase in the volume of the gas in one infinitesimal step.

The total amount of work done by the gas during isothermal and reversible expansion from volume V_1 to V_2 can be obtained by integration.

$$w = -\int_{V_1}^{V_2} p.dV$$

Since, for an ideal gas $pV = nRT$,

we have,

$$w_{rev} = -\int_{V_1}^{V_2} \frac{nRT}{V}.dV = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

or $\boxed{w_{rev} = -2.303\, nRT \log_{10} \dfrac{V_2}{V_1}}$

Moreover, for an ideal gas

$$p_1V_1 = p_2V_2 \text{ i.e., } \frac{V_2}{V_1} = \frac{p_1}{p_2}$$

Therefore,

$\boxed{w_{rev} = -2.303nRT\log_{10}\dfrac{p_1}{p_2}}$

3. **Although heat is a path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.** **[NCERT Exemplar]**

Ans. The conditions under which heat becomes independent of path are;

(a) If volume remains constant

(b) If pressure remains constant

At constant volume: $\Delta V = 0$. Thus, $\Delta U = q + p\Delta V = q$.
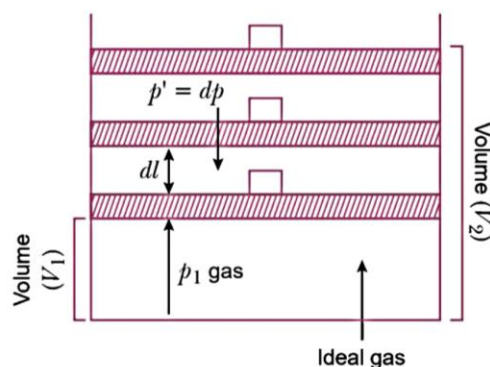
Since ΔU is a state function.

$\therefore$ q_v is a state function.

Similarly,

**At constant pressure:** $\Delta U = q_p - p\Delta V$ (if work is done by the system)

$q_p = \Delta U + p\Delta V = \Delta H$ is a state function.

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4. **What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in Figure given below. Explain graphically.** *[NCERT Exemplar] [HOTS]*
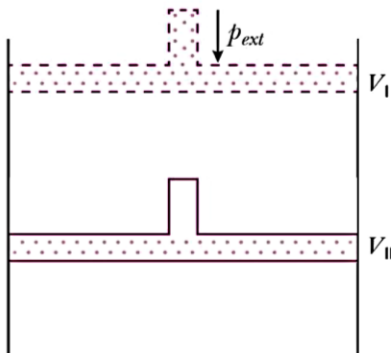
Ans. Let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. If external pressure is p_{ext} which is greater than p, piston is moved inward till the pressure inside becomes equal to p_{ext}. Let this change be achieved in a single step and the final volume be V_f.
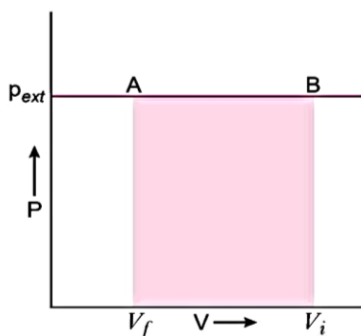
If work (W) is done on the system, then

$$W = -p_{ext}(V_f - V_i)$$

This work is equal to the shaded area $AB\, V_f V_i$.

5. **How will you calculate work done on an ideal gas in a compression, when change in pressure is carried out in infinite steps?** *[NCERT Exemplar]*

Ans. A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change.

Work done can be calculated from pV-plot where pressure is not constant and changes are in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.

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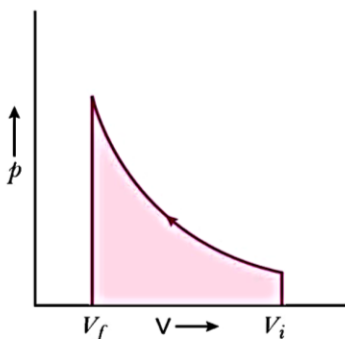
6. **1.0 mol of a monoatomic ideal gas is expanded from state (1) to state (2) as shown in figure given below. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K.** [*NCERT Exemplar*] [*HOTS*]
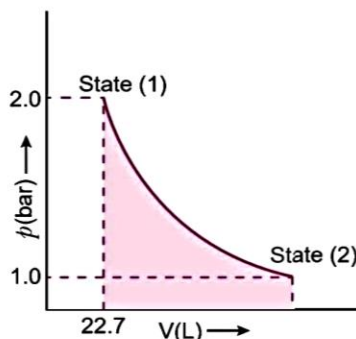
Ans. From the given diagram, it is very clear that it is a isothermal reversible change because the process is carried out in the no. of steps.

$$w = -2.303 \, nRT \log \frac{V_2}{V_1}$$

But, $p_1 V_1 = p_2 V_2 \implies \dfrac{V_2}{V_1} = \dfrac{p_1}{p_2} = \dfrac{2}{1} = 2$

$\therefore \quad w = -2.303 \, nRT \log \dfrac{p_1}{p_2}$

$= -2.303 \times 1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} \times \log 2$

$= -2.303 \times 8.314 \times 298 \times 0.3010 \text{ J} = \mathbf{-1717.46 \text{ J}}$

7. **With the help of first law of thermodynamics and $H = U + pV$, prove $\boxed{\Delta H = q_p}$**

Ans. The enthalpy is the sum of internal energy and product of pressure and volume

$H = U + pV$

For a change in the states of system,

$\Delta H = \Delta U + \Delta(pV)$

$\Delta H = \Delta U + \Delta pV + p\Delta V$ ...(i)

From first law of thermodynamics

$\Delta U = q + w$

$= q - p.\Delta V$ ...(ii)
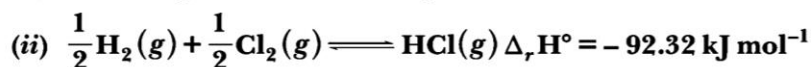
From equation (i) and (ii)

$\Delta H = q - p.\Delta V + \Delta pV + p.\Delta V$

$\Delta H = q + \Delta p.V$

when pressure is constant, $\Delta p = 0$, so
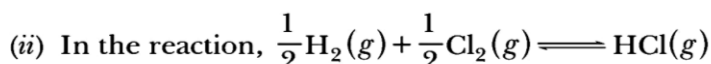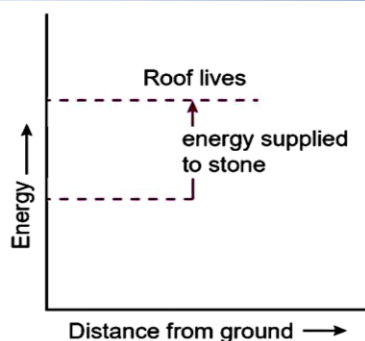
$\boxed{\Delta H = q_p}$

8. **Represent the potential energy/enthalpy change in the following processes graphically.**
   **(i) Throwing a stone from the ground to roof.**

   (ii) $\dfrac{1}{2} H_2(g) + \dfrac{1}{2} Cl_2(g) \rightleftharpoons HCl(g) \, \Delta_r H^\circ = -92.32 \text{ kJ mol}^{-1}$

   In which of the processes potential energy/enthalpy change is contributing factor to the spontaneity? [*NCERT Exemplar*]

Ans. (i) On throwing stone from ground to the roof we need to supply energy to the stone and thus, energy increases.

Graphically, it can be represented as

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(*ii*) In the reaction, $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightleftharpoons HCl(g)$

Heat is evolved it means the process is followed by decrease in energy.
It can be represented as
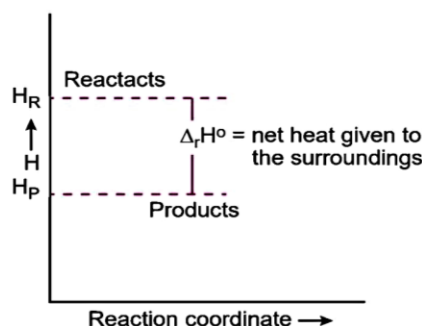
Therefore in process (*b*), the enthalpy change is the contributing factor to the spontaneity.

9. The ΔH and ΔS for the reaction $2Ag_2O(g) \longrightarrow 4Ag(s) + O_2(g)$ are given as -61.17 kJ mol^{-1} and $+132$ JK^{-1} mol^{-1} respectively. Above what temperature will the reaction be spontaneous?

Ans. The reaction,

$$2Ag_2O(g) \longrightarrow 4Ag(s) + O_2(g) \text{ will be spontaneous when } \Delta G = -\text{ve.}$$
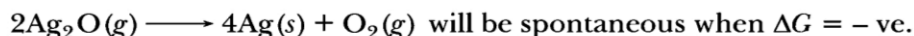
From the given data

$$\Delta H = -\text{ve and } \Delta S = +\text{ve}$$

So, by the relation

$$\Delta G = \Delta H - T.\Delta S$$

ΔG would be $-$ve

if $\quad \Delta H < T.\Delta S$

or $\quad T > \dfrac{\Delta H}{\Delta S} = \dfrac{61170 \text{ J mol}^{-1}}{132 \text{ JK}^{-1} \text{ mol}^{-1}}$

$T > 463.4$ K

$\therefore$ This reaction will be spontaneous above a temperature of 463.4 K.

10. Show that the work done by a system is not a state function.

Ans. Work done in isothermal and reversible expansion of an ideal gas is

$$\boxed{w_{rev} = -2.303 \, nRT \log_{10} \dfrac{p_1}{p_2}}$$

Work done in isothermal and irreversible expansion of a gas

$$w_{irrev} = -p_2 \int_{V_1}^{V_2} dV$$

or $w_{irrev} = -p_2(V_2 - V_1)$

The work done in the isothermal and irreversible expansion of a gas is always smaller than the work done in the isothermal and reversible expansion of the gas. This implies that the work done by a system is not a state function. The work is related to the manner in which the process is carried out rather than to the initial and final states of the system.

LONG ANSWER QUESTIONS (5 marks)

1. Derive the relationship between ΔH and ΔU for an ideal gas. Explain each term involved in the equation. *[NCERT Exemplar]*

Ans. Derivation: Let us consider, a reaction which involves gases and occurs at a constant pressure p and at constant temperature T. Let V_A be the total volume of gaseous reactants and V_B the total volume of gaseous products. If n_A is the total number of moles of gaseous reactants and n_B is the total number of moles of gaseous products, then according to the ideal gas equation we have,

$$pV_A = n_A RT$$

and $pV_B = n_B RT$

$\therefore$ $p(V_B - V_A) = (n_B - n_A)RT$

$p\Delta V = \Delta n_g RT$ ...(i)

Now, Enthalpy (H) is regarded as the total heat content of a system at constant pressure.

Mathematically, $H = U + pV$

where, U is the internal energy of the system. p and V represent the pressure and volume of the system respectively. Enthalpy is a state function.

Therefore,

$$\Delta H = H_{\text{Products}} - H_{\text{Reactants}}$$

Now, from first law of thermodynamics

$\Delta U = q_p - p.\Delta V$

We can rewrite the above equation as

$U_2 - U_1 = q_p - p(V_2 - V_1)$

On rearranging, we get

$q_p = (U_2 + pV_2) - (U_1 + pV_1)$

Thus, $U_2 + pV_2 = H_2$ and

$U_1 + pV_1 = H_1$

Hence, $\Delta H = q_p$

or $\Delta H = \Delta U + \Delta(pV)$

$\Delta H = \Delta U + p.\Delta V + V.\Delta p$

If a change takes place at constant pressure (*i.e.*, $\Delta p = 0$), then we have

$$\boxed{\Delta H = \Delta U + p.\Delta V}$$ ...(ii) at constant pressure

Now putting the value of $p.\Delta V$ from equation (i) in equation (ii), we get

$$\boxed{\Delta H = \Delta U + \Delta n_g RT}$$

where ΔH = change in enthalpy

ΔU = change in internal energy

Δn_g = no. of moles of gaseous products – no. of moles of gaseous reactants

R = Gas constant

T = Temperature

2. **Extensive properties depend on the quantity of matter but intensive properties do not. Explain whether the following properties are extensive or intensive.**

Mass, internal energy, pressure, heat capacity, molar heat capacity, density, mole fraction, specific heat, temperature and molarity. [*NCERT Exemplar*]

Ans. The properties which depend upon the quantity of the substance present in the system are termed as extensive properties. On the other hand, the properties which are independent of the quantity of the substance present in the system are called intensive properties. properties. The ratio of two extensive properties is always intensive. Therefore, the given properties can be classified as:

Intensive Properties	Extensive Properties
Pressure, mole fraction, molarity, molar heat capacity, density, specific heat and temperature	Mass, internal energy and heat capacity

3. **Use the following data to calculate $\Delta_{lattice} H^{\ominus}$ for NaBr.**

$\Delta_{sub} H^{\ominus}$ **for sodium metal = 108.4 kJ mol^{-1}**

Ionization enthalpy of sodium = 496 kJ mol^{-1}

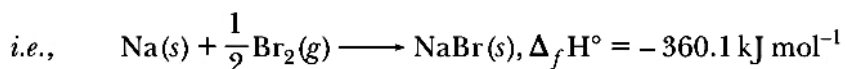**Electron gain enthalpy of bromine = –325 kJ mol^{-1}**

Bond dissociation enthalpy of bromine = 192 kJ mol^{-1}

$\Delta_f H^{\ominus}$ **for NaBr(s) = – 360.1 kJ mol^{-1}** [*NCERT Exemplar*]

Ans. Calculation of Lattice enthalpy of NaBr(s) from Born-Haber cycle.

The ΔH_f (heat of formation) of NaBr(s) = – 360.1 kJ mol^{-1}

i.e., $\quad Na(s) + \dfrac{1}{2} Br_2(g) \longrightarrow NaBr(s), \Delta_f H^{\circ} = - 360.1 \, kJ \, mol^{-1}$

1 mole of NaBr(s) can be prepared by the following steps:

(i) Sublimation of sodium metal

$\quad Na(s) \longrightarrow Na(g), \qquad\qquad \Delta_{sub} H^0 = S = 108.4 \, kJ/mol$

(ii) Dissociation of Cl$_2$ molecule in gaseous atoms

$\quad \dfrac{1}{2} Br_2(g) \longrightarrow Br(g), \qquad\qquad \dfrac{1}{2}\Delta_{bond} H^0 = \dfrac{1}{2}D = \dfrac{192}{2} kJ/mol$

(iii) Ionisation of gaseous Na atoms

$\quad Na(g) \longrightarrow Na^+(g) + e^- \qquad\qquad \Delta_i H^0 = I.E. = 496 \, kJ/mol$

(iv) Formation of gaseous bromide ions

$\quad Br(g) + e^- \longrightarrow Br^-(g), \qquad\qquad \Delta_{eg} H^0 = E.A = -325 \, kJ/mol$

(v) Formation of 1 mole of NaBr

$\quad Na^+(g) + Br^-(g) \longrightarrow NaBr(s), \qquad \Delta_{lattice} H^0 = -U$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ (lattice enthalpy)

Born-Haber Cycle

$$Na(s) + \frac{1}{2}Br_2(g) \xrightarrow{\Delta_f H^\circ} NaBr(s)$$
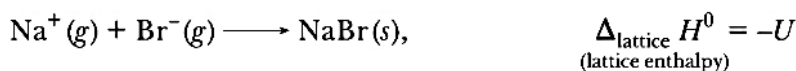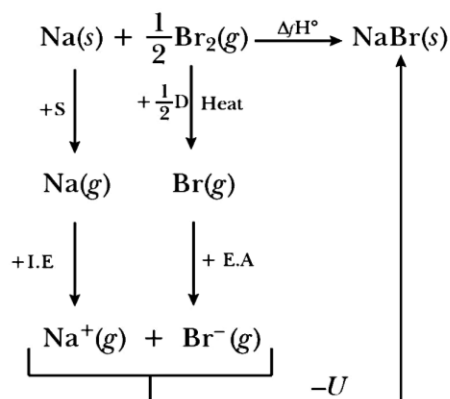
By applying Hess's law

$$\Delta_f H^\circ = S + \frac{1}{2}D + I.E + E.A + U$$

$$-360.1 = 108.4 + 96 + 496 + (-325) - U$$

Thus, $\qquad U = + 735.5 \text{ kJ/mol}$

4. **ΔG is net energy available to do useful work and is thus a measure of "free energy". Show mathematically that ΔG is a measure of free energy. Find the unit of ΔG. If a reaction has positive enthalpy change and positive entropy change, under what condition will the reaction be spontaneous?** [NCERT Exemplar]

Ans. The maximum amount of energy available to a system during a process for doing useful work under constant temperature and pressure conditions is called Gibbs free energy.

From first law of thermodynamics,

$q = \Delta U + w_{\text{expansion}} + w_{\text{non-expansion}}$

At constant pressure, $w_{\text{expansion}} = p.\Delta V$

$q = \Delta U + p\Delta V + w_{non\text{-}expansion}$ $\qquad (\because \Delta H = \Delta U + p\Delta V)$

$q = \Delta H + w_{non\text{-}expansion}$ $\qquad$ ...(i)

For a reversible change taking place at constant temperature

$\qquad \Delta S = \dfrac{q_{rev}}{T}$

or $\qquad q_{rev} = T\Delta S$ $\qquad$ ...(ii)

Putting the value of q_{rev} in equation (i) we get

$\qquad T.\Delta S = \Delta H + w_{\text{non-expansion}}$

or $\quad \Delta H - T\Delta S = -w_{\text{non-expansion}}$ $\qquad$ ...(iii)

For a change taking place under conditions of constant temperature and pressure,

$\qquad \Delta G = \Delta H - T\Delta S$ $\qquad$ ...(iv)

Substituing this value in equation (iii), we get

$\qquad \Delta G = -w_{\text{non-expansion}}$

Thus, free energy is a measure of the useful or net work derived during the change.

ΔG has the same units as those of work *viz* joule.

From $\quad \Delta G = \Delta H - T.\Delta S$

If $\qquad \Delta H = +$ve and $\Delta S = +$ve, then

ΔG will be negative and process will be spontaneous when $T.\Delta S > \Delta H$, which will be so when temperature (T) is high.

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5. What are the different Thermodynamic processes?

Ans. A thermodynamic process is said to occur when the system changes from one state (initial state) to another (final state).

A thermodynamic system may undergo following types of processes.

(*i*) **Isothermal process:** The process occurring at constant temperature is termed as an isothermal process *i.e.*, for such a process $\Delta T = 0$.

(*ii*) **Adiabatic process:** The process in which no heat is exchanged between the system and the surroundings is called an adiabatic process *i.e.*, for such a process $\Delta q = 0$

(*iii*) **Isochoric:** The process occurring at constant volume is known as an isochoric process *i.e.*, for such a process $\Delta V = 0$.

(*iv*) **Isobaric process:** The process occuring at constant pressure is termed as an isobaric process *i.e.*, for such a process $\Delta p = 0$

(*v*) **Cyclic process:** When initial and final point in a process are the same, the process is called a cyclic process *i.e.*, For such a process $\Delta V = 0$ and $\Delta H = 0$.

6. State the first law of thermodynamics. Write its mathematical formulation. How would you justify this law?

Ans. The first law of thermodynamics is simply the law of conservation of energy. It can be stated as:

"Energy can neither be created nor destroyed although it can be converted from one form to another."

Mathematical formulation of the first law of thermodynamics.

The internal energy of a system can be increased in two ways

(*i*) By supplying heat to the system.

(*ii*) By doing work on the system.

Suppose the initial internal energy of the system = U_1.

If it absorbs heat q, its internal energy will become = $U_1 + q$

If further work is done on the system, internal energy will further increase and become = $U_1 + q + w$.

Let us assume this final internal energy as U_2.
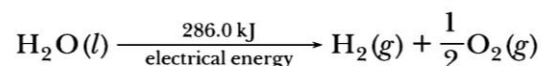
Then, $U_2 = U_1 + q + w$
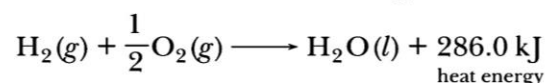
or $U_2 - U_1 = q + w$

$$\boxed{\Delta U = q + w}$$

This equation is the mathematical formulation of the first law of thermodynamics.

Justification for the first law of thermodynamics.

On supplying 286.0 kJ of electrical energy to one mole of water, it decomposes to give one mole of hydrogen and half mole of oxygen.

$$H_2O\,(l) \xrightarrow[\text{electrical energy}]{286.0 \text{ kJ}} H_2\,(g) + \frac{1}{2}O_2\,(g)$$

If one mole of hydrogen is allowed to burn in half mole of oxygen, one mole of water is formed and the same amount of energy in the form of heat is liberated.

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l) + 286.0 \text{ kJ}_{\text{heat energy}}$$

This example clearly indicates that the energy is always conserved though it may change its form.

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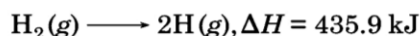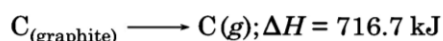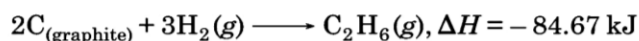STUDY CIRCLE
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QUESTIONS FOR PRACTICE

1. State first law of thermodynamics. Write its mathematical formula.

2. When is the entropy of a perfectly crystalline solid approaches zero?

3. What do you understand by the term Thermodynamic equilibrium?

4. What is the relationship between ΔH and ΔU for the process.

   $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$?

5. Although dissolution of ammonium chloride in water is endothermic, but still it dissolves in water readily. Why ?

6. Define heat and work and mention their sign conventions.

7. Comment on the spontaneity of a process when

   (i) $\Delta H < 0, T.\Delta S > 0$ (ii) $\Delta H > 0, T.\Delta S < 0$

   (iii) $\Delta H > 0, T.\Delta S > 0$ and $T.\Delta S < \Delta H$ (iv) $\Delta H < 0, T\Delta S < 0$ and $T.\Delta S > \Delta H$

8. Calculate the calorific value of sugar, if its heat of combustion is 5645 kJ mol^{-1}.

9. Show that $\Delta G = -T\Delta S$total.

10. Calculate the entropy change ($\Delta S°$) for the following reaction at 25°C.

    $$SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$$
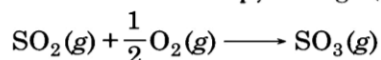
    The absolute entropies at 25°C and 1 atm pressure for SO2(g), O2(g) and SO3(g) are 248.5, 205.0 and 256.2 JK–1 mol–1 respectively.

11. (i) Define Bond enthalpy.

    (ii) Calculate the C–C bond energy from the following data.

    $$2C_{(graphite)} + 3H_2(g) \longrightarrow C_2H_6(g), \Delta H = -84.67 \text{ kJ}$$

    $$C_{(graphite)} \longrightarrow C(g); \Delta H = 716.7 \text{ kJ}$$

    $$H_2(g) \longrightarrow 2H(g), \Delta H = 435.9 \text{ kJ}$$

    Assume 416 kJ as the C–H bond energy.

Answers

4. $\Delta H = \Delta U$, because $\Delta n_g = 0$ 8. 16.5 kJ/g   10. –94.8 J/K/mol

11. (ii)329.77 kJ mol^{-1}